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# **KINETICS OF COLLOIDAL SILICA GELATION AT EGS CONDITIONS AND IMPLICATIONS FOR RESERVOIR MODIFICATION**

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## **ABSTRACT**

Fractures and fracture networks are the principal pathways for migration of water and contaminants in groundwater systems, fluids in enhanced geothermal systems (EGS), oil and gas in petroleum reservoirs, carbon dioxide leakage from geological carbon sequestration, and radioactive and toxic industrial wastes from underground storage repositories. In EGS fracture networks, there are several major issues to consider, e.g., the minimization of hydraulic short circuits and losses of injected geothermal fluid to the surrounding formation, which in turn maximize heat extraction and economic production. Gel deployments to direct and control fluid flow have been extensively and successfully used in the oil industry for enhanced oil recovery, and to divert and contain radioactive and toxic wastes. However, to the best of our knowledge, gels have not been applied to EGS to enhance heat extraction. Inorganic gels, such as colloidal silica gels, may be ideal blocking agents for EGS systems if suitable gelation times and control of gelation behavior can be achieved. In the current study, we explore colloidal silica gelation times, rheology, and gel stability as a function of SiO<sub>2</sub> concentration, pH, salt concentration, and temperature up to 300 °C. Results at 25 °C show that it may be possible to choose formulations that will gel in a reasonable and predictable amount of time at EGS temperatures. Results at EGS temperatures indicate that usage of colloidal silica gels may be limited in very high-temperature reservoirs, but may be ideal for reservoir modification at low to medium EGS conditions.

## **INTRODUCTION**

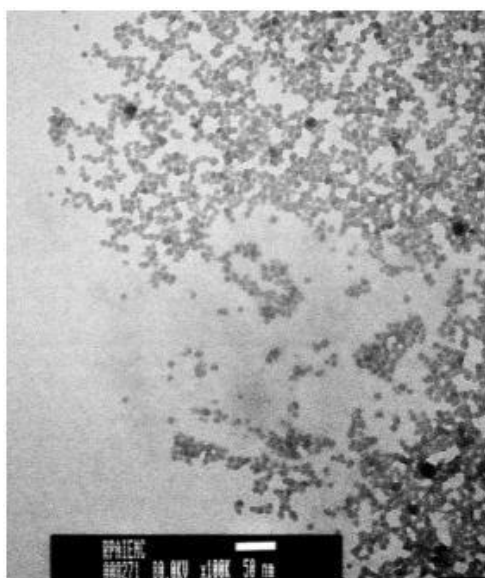
In enhanced geothermal systems (EGS) the reservoir permeability is often enhanced or created using hydrofracking. In hydrofracking, high fluid pressures are applied to confined zones in the subsurface, usually using packers, to fracture the host rock. This enhances rock permeability and therefore conductive heat transfer to the circulating geothermal fluid (e.g. water or supercritical carbon dioxide). The ultimate goal is to increase or improve the thermal energy production from the subsurface by either optimal designs of

injection and production wells or by altering the fracture permeability to create different zones of circulation that can be exploited in geothermal heat extraction. Moreover, hydrofracking can lead to the creation of undesirable short-circuits or fast flow-paths between the injection and extraction wells, leading to a short thermal residence time, low heat recovery, and thus a short-life of the EGS.

A potential remedy to these problems is to deploy a cementing (blocking, diverting) agent to minimize short-cuts and/or create new circulation cells for heat extraction. A potential diverting agent is the colloidal silica by-product that can be co-produced from geothermal fluids. Silica gels are abundant in various surface and subsurface applications, yet they have not been evaluated for EGS applications. While it is unlikely that colloidal silica gels have the strength required to block one zone while another is stimulated during the initial hydrofracking, silica gel deployment may have a beneficial effect on the thermal response of an EGS (or any geothermal field) during normal operation. This may be through blocking short-circuiting undesirable pathways as a result of diverting the geofluid to other fractures, or creating, within fractures, new circulation cells for harvesting heat through newly active surface area contact. A significant advantage of colloidal silica is that it can be co-produced from geothermal fluids as a colloidal sol using an inexpensive membrane-based separation technology that was developed previously (Bourcier et al., 2008).

This co-produced colloidal sol has properties that potentially make it useful as a fluid diversion agent for subsurface applications. Silica sols are suspensions of colloidal silica that exist as a low-viscosity liquid and are stable for long periods of time. When the sols are destabilized, using pH changes, addition of salt, and/or increasing the temperature, microscopic regions of gel start to form (microgels), in which the water becomes the suspended phase within a network of bonded colloids. Once enough microgel regions form, they increase the viscosity of the solution as they interact, merge, and eventually develop into a continuous network (Iler, 1979). On a macroscopic level, this means that the solutions exist as low-viscosity fluids during their “induction period” but then undergo a rapid increase in viscosity (gelation) to form a solid gel. The length of the induction period can be manipulated by varying the properties of the solution, such as silica concentration and colloid size, pH, and salt concentration. We believe it is possible to produce colloidal silica solutions suitable for use as diverting agents for blocking undesirable fast-paths which result in short-circuiting the EGS once hydrofracking has been deployed. In addition, the gels could be used in conventional geothermal fields to increase overall energy recovery by modifying flow.

We believe there may be additional advantages for using colloidal silica as blocking agents. It can be inexpensively produced on site or at other geothermal sites (Figure 1); it is inorganic and environmentally friendly as opposed to organic gels often used in oil/gas industry, and, unlike conventional blocking agents, the gel material might be hydraulically removed after emplacement. Furthermore, colloidal silica gelation can be triggered externally, for example by mixing with salt solutions or changing the pH in the subsurface; there should be fewer environmental restrictions and permitting requirements for its use given that the material originates in the same place it is to be injected, and silica removal in itself benefits the power plant in terms of silica scale control.



*Figure 1: Silica gel produced from the Mammoth Lakes geothermal fluid. The gel is made up of a network of 10nm silica colloids.*

To accurately predict when an injected geothermal fluid will set up and turn to gel, a quantitative understanding of the kinetics of silica gelation is required. Although silica gels have been studied for decades, much of the recent literature investigates dry silica gels for their adsorbent properties, and even the most comprehensive resources (Iler, 1979; Bergna and Roberts, 2006) provide only a qualitative understanding of the various factors (pH, salt concentration, temperature, colloid diameter,  $\text{SiO}_2$  concentration, etc.) that influence gelation times from an initial sol. Furthermore, much of the research on colloidal silica has been performed by the oil and gas and other industries (e.g., Jurinak and Summers, 1991; Vossoughi, 2000), and is, therefore, mostly proprietary. We did not

find any quantitative method or model for predicting gel times from colloidal silica compositions. Such a method is needed to develop formulations for colloidal silica solutions for given geothermal applications. In addition, there is very little information on gelation kinetics at elevated temperatures. Because of these needs, we began an effort to acquire additional data that could be combined with the existing data to develop a more comprehensive quantitative model for use in our geothermal application.

However, colloidal silica gel is thermodynamically unstable relative to the stable phase assemblage of quartz and water, or even a metastable assemblage of amorphous silica and water. This is not an issue at low temperatures, where the activation energy and kinetics of the aggregation process hinder the formation of amorphous silica over any industry-relevant timescale. At high temperatures, however, the activation energy is more readily reached and the process is therefore hastened to the point that gel stability becomes a concern over relevant timescales. We have therefore begun an investigation into the thermal stability of colloidal silica gels in aqueous environments.

## **METHODS**

For our initial experiments at 25 °C, we used a Sunshine Instruments Gel Time Meter (Figure 2).



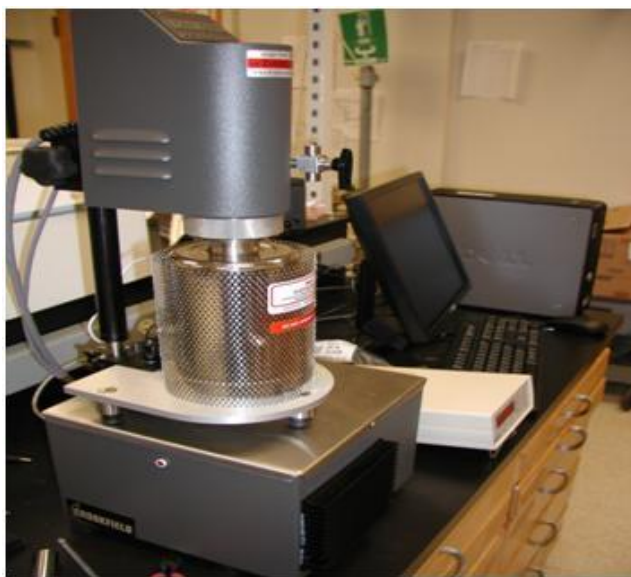
*Figure 2: Sunshine Instruments Gel Time Meter*

*(<http://www.davis.com>)*

To use the Gel Time Meter, a sample is placed into a small polyethylene centrifuge tube which is, in turn, set in a water bath. The temperature can be controlled within 1 °C. A stir rod is hung from a torsion wire and immersed into

the sample, which will rotate when the power to the meter is turned on. Turning the power on also starts a time counter. The lower and upper electrical contacts are set  $\sim 1$  cm apart. The viscosity of the sample creates a drag on the rotation of the stir rod and the lower electrical contact, bringing the two contacts closer together. At a certain threshold viscosity, based on the torque on the torsion wire required to bring the lower and upper electrical contacts together, the meter and counter shut off, recording the number of seconds between turning the meter on and reaching the threshold viscosity. This provides an accurate report of the gelation time of aqueous silica sols. The water bath can be used to bring the samples above ambient temperature, but because the stir rod must be lowered into the sample for the duration of the test, the water in the sample may escape due to evaporation or boiling. Therefore, we limited our experiments in the Gel Time Meter to below  $85^{\circ}\text{C}$ .

The second instrument used in our experiments is a PVS rheometer from Brookfield Engineering, for experiments at elevated conditions (Figure 3). The PVS rheometer has an enclosed sample chamber, preventing sample boil-off. It can be operated up to  $200^{\circ}\text{C}$  and 1000 psi (6.9 MPa), and can provide an accurate, quantitative measure of sample viscosity as a function of time and/or shear rate, by measuring the torque exerted on an inner cylinder inside the sample chamber. The instrument enables measurement of both simple gelation times as well as non-Newtonian behavior, e.g., thixotropy, of colloidal silica sols and gels.



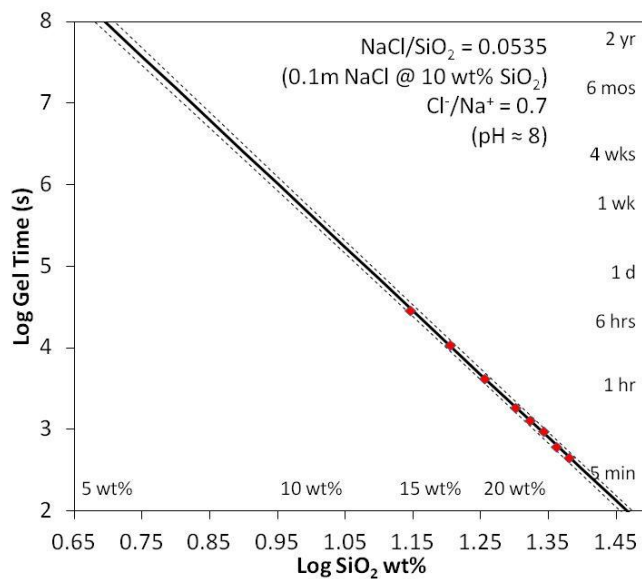
*Figure 3: PVS Rheometer from Brookfield Engineering (<http://www.brookfieldengineering.com>)*

Experiments exploring gelation times and the thermal stability of the gel at EGS conditions (150-300 °C) were done using steel capsules by Swagelok. Leak tests showed no water loss after four days at 275 °C. State of the gel was determined via physical observation upon quenching the capsule in water. Using this method, it is necessary to perform multiple experiments at the same temperature and composition for different durations in order to bracket the transition time from sol to gel and the time to gel destabilization.

## **RESULTS AND DISCUSSION**

### **Gel Time Meter, 25 °C**

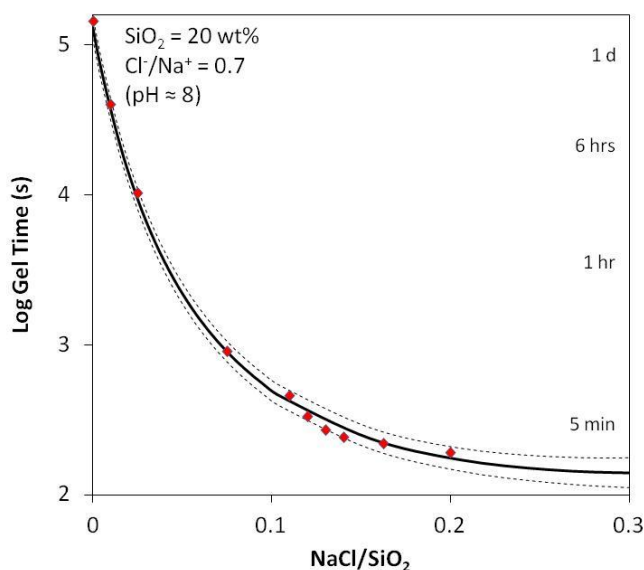
The gel time meter was used to quantitatively determine the effects of SiO<sub>2</sub> concentration, pH, and salt concentration on the gelation time of colloidal silica sols made with commercially available LUDOX SM-30 at 25 °C, to provide a foundation for experiments at higher temperature. The major finding of this investigation is that there is a simple and clear relationship between gelation time and SiO<sub>2</sub> concentration. Previous investigations varied SiO<sub>2</sub> concentration while keeping pH and NaCl concentration constant. However, if the dilution is done by adding different amounts of water to identical mixtures of colloidal silica sol, NaCl, and HCl, a linear relationship arises between the logarithm of gelation time and the logarithm of the silica concentration (Figure 4). While the NaCl concentration and pH are changing as the mixtures become more diluted, the molar ratio of NaCl to SiO<sub>2</sub> and the molar ratio of added HCl to the Na<sup>+</sup> stabilizer present in the colloidal sol (hereafter referred to as Cl<sup>-</sup>/Na<sup>+</sup> ratio) remain constant.





*Figure 4: Log gel time vs. log silica concentration. Dashed lines are 95% confidence intervals over the entire model.*

The relationship between gelation time and the molar NaCl/SiO<sub>2</sub> ratio is more complex. Increasing the amount of salt, while keeping all other variables constant, initially has a large, decreasing effect on gelation time, but as more salt is added, the effect is diminished. However, the addition of salt always decreases the gelation time. This has been modeled as a modified hyperbolic relationship (Figure 5).



*Figure 5: Log gel time vs. NaCl/silica ratio (NaCl created from the neutralization of Na<sup>+</sup> stabilizer with HCl is not included in this ratio). Dashed lines are 95% confidence intervals over the entire model.*

The relationship between gelation time and Cl<sup>-</sup>/Na<sup>+</sup> ratio is more complex still, as there are competing rate-limiting steps at low pH and high pH. Nevertheless, at near-neutral pH (6-9; Cl<sup>-</sup>/Na<sup>+</sup> ratio = 0.5-1), the relationship can be modeled as a parabola (Figure 6).

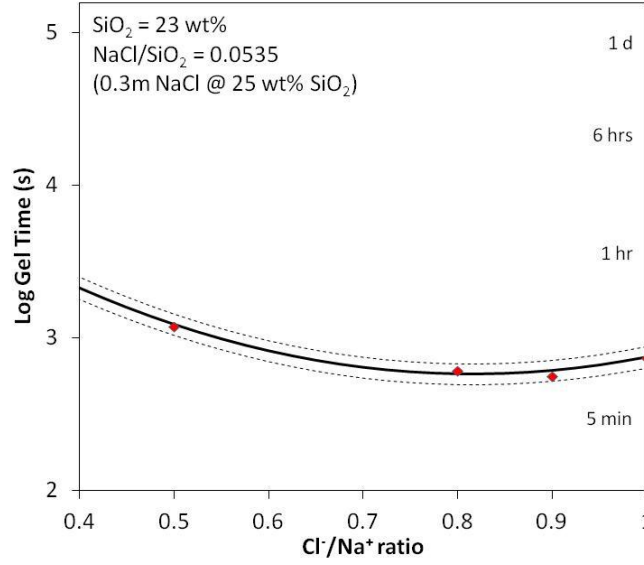


Figure 6: Log gel time vs.  $Cl^-/Na^+$  ratio (added NaCl is not included in this ratio). Dashed lines are 95% confidence intervals over the entire model.

The entire dataset (91 experiments) was fitted to a single equation with 11 regression parameters, as a function of  $SiO_2$  wt%, molar  $NaCl/SiO_2$  ratio ( $NaCl$  formed via neutralization of the  $Na^+$  stabilizer is not included in this ratio), and molar  $Cl^-/Na^+$  ratio (added  $NaCl$  is not included in this ratio). The dashed lines in each of Figures 4-6 represent the 2 standard deviation error for the entire regression. The regression equation ( $R^2 = 0.9973$ ) is as follows:

$$\log(Gel\ Time\ (s)) = A \times \log(SiO_2\ wt\%) + B \quad (1)$$

where A and B are defined as follows:

$$A = \frac{NaCl}{SiO_2} \left( A_1 \left( \frac{Cl^-}{Na^+} \right)^2 + A_2 \left( \frac{Cl^-}{Na^+} \right) + A_3 \right) + A_4 \left( \frac{Cl^-}{Na^+} \right)^2 + A_5 \quad (2)$$

$$B = \left( \frac{NaCl}{SiO_2} + B_1 \right)^{-1} \left[ B_2 \left( \frac{Cl^-}{Na^+} \right)^2 + B_3 \right] + B_4 \frac{NaCl}{SiO_2} + B_5 \left( \frac{Cl^-}{Na^+} \right) + B_6 \quad (3)$$

The numerical values of  $A_1$ - $A_5$  and  $B_1$ - $B_6$  are given in Table 1, and the error between prediction and measurement for each experiment is shown in Figure 7. No systematic error was observed over  $\text{SiO}_2$  concentration,  $\text{Cl}^-/\text{Na}^+$  ratio,  $\text{NaCl}/\text{SiO}_2$  ratio, or observed gelation time. While most of the parameters were fitted by linear regression, it was not possible to fit parameter  $B_1$  linearly. It therefore was fitted with non-linear regression (iterative use of Excel's solver and linear regression functions) to maximize the value of  $R^2$ , and does not have a well-defined error.

Table 1: Fitting Parameters for Equation 1.

Parameter	Value	Error ( $1\sigma$ )
$A_1$	-15.24	1.729
$A_2$	26.08	2.585
$A_3$	4.58	1.474
$A_4$	5.40	0.202
$A_5$	-11.25	0.184
$B_1$	0.066	N/A
$B_2$	-0.356	0.014
$B_3$	0.461	0.010
$B_4$	-18.03	1.415
$B_5$	-7.21	0.313
$B_6$	17.02	0.293

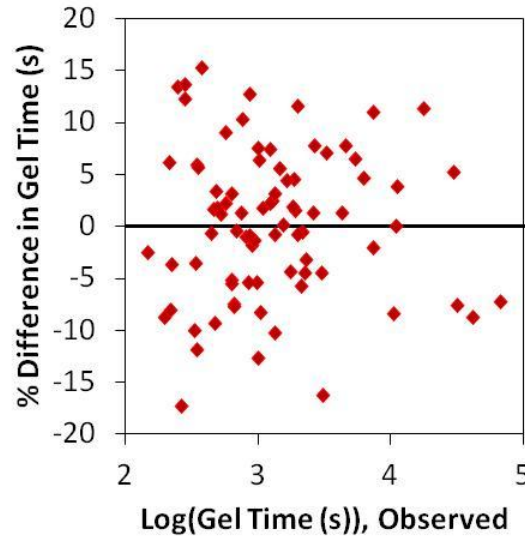
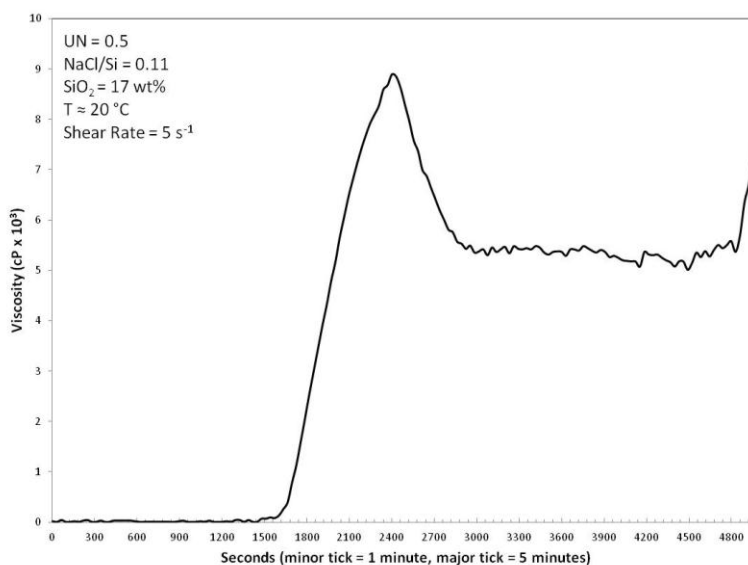


Figure 7: % Difference in Gel Time (s) between Predicted and Observed values vs. Observed Log(Gel Time).

### Rheological Properties of Silica Gel

Preliminary results from the rheometer indicate that gelation times can be reliably obtained from plots of viscosity over time, and that shear rate does not affect gelation time. An example of a viscosity over time plot is shown on Figure 8.



*Figure 8: Viscosity (cP x 10<sup>3</sup>) as a function of time (seconds), measured at room temperature at a constant shear rate of 5 s<sup>-1</sup>.*

The data in Figure 8 are for a colloidal silica solution with 17 wt% SiO<sub>2</sub>, a NaCl/SiO<sub>2</sub> ratio of 0.11, and a Cl<sup>-</sup>/Na<sup>+</sup> ratio of 0.5, subjected to a continuous shear rate of 5 s<sup>-1</sup> at 20 °C. The viscosity remained near that of pure water for approximately 1600 seconds, which agrees well with the gelation time of 1634 seconds recorded by the gel time meter for the same colloidal silica solution. During the gelation process, the colloidal solution starts thickening, the viscosity increases significantly, and reaches a maximum of 9000 cP at around 2400 seconds. After this point, the gel starts to slip past the inner cylinder rather than exerting a constant torque on it, causing the measured viscosity to drop and become irregular. However, the gel itself continues to stiffen and become brittle. Therefore, the information gathered after the maximum viscosity reached is irrelevant to this investigation.

This experiment was repeated using several different shear rates. The measured gelation time for each shear rate was within 2-3 minutes of the measured gelation time in the gel time meter; however, the maximum

viscosity was dependent on the shear rate. If the shear rate doubles, the maximum viscosity recorded will be halved. This is entirely due to the interfacial layer of gel/water at the inner cylinder, and not reflective of the actual viscosity of the bulk gel as a whole. Therefore, at least in this experimental geometry, shear rate is not a significant variable when determining the gelation time.

### **EGS Conditions**

We have investigated the effect of temperature on gelation time using the gel time meter (below 85 °C) and phase-bracketing experiments at higher temperatures. It is well-known that gelation time follows an Arrhenius relationship, but due to the large variety of possible silica sol compositions, colloid sizes, and other factors, the values for the activation energy associated with the relationship vary widely within the literature, between 5 and 20 kcal/mol. It is also well-known that the thermodynamically stable phase assemblage at EGS conditions is quartz and water, though deposition of amorphous silica is typically favored due to nucleation barriers. In either case, the gel structure may not be thermally stable for long periods of time. We therefore have also investigated the thermal stability of the gel at EGS conditions. Figure 9 shows gel times for a single solution composition (15% SiO<sub>2</sub>, no added NaCl, Cl<sup>-</sup>/Na<sup>+</sup> = 0.5) measured from 65-85 °C in the gel time meter, brackets of the gelation time from 150-300 °C, and brackets of the time required for amorphous silica deposition. There is significantly more scatter in the gel time meter experiments at high temperature than in those at ambient conditions, which we attribute to variable evaporation of the sample. The activation energy for silica gelation shown in Figure 9 falls within the accepted range of literature activation energies, at  $10.7 \pm 0.5$  kcal/mol ( $44.8 \pm 2.1$  kJ/mol). It should be noted that the activation energy of gelation reported here is not the true activation energy. Iler (1979) reports that as colloidal solutions are heated, the colloids grow in size to an equilibrium value. Independently from temperature, the size of the colloids will affect the gelation time. Because the growth of colloids at a constant concentration of silica means there is a smaller number of colloids per unit volume of solution, this will actually lengthen the gelation time. The true activation energy of the gelation mechanism can only be measured for a colloidal solution with colloids larger than the ultimate equilibrium value in the experiment. Nevertheless, EGS applications would only require the total effect of temperature on a given initial colloidal solution composition, which is what is reported here.

The transition from gel to amorphous silica and water is not abrupt. As the gel ages, it transitions from a clear solid to a white solid, as microscopic regions of the gel become more concentrated in silica and start to refract

light. The gel then shrinks slightly and starts to expel water. When enough water is expelled, the gel structure collapses and turns into a turbid, milky fluid. As the fluid is allowed to age further, the amorphous silica particles settle out and the water becomes transparent. Figure 9 therefore shows a broad transition zone from the gel phase to amorphous silica and water. The activation energy for the deposition of amorphous silica is significantly higher than the activation energy of gelation, at  $22.3 \pm 2.2$  kcal/mol. At relatively low EGS temperatures, this means that the gel will be stable for a significant amount of time, e.g., at 100 °C, the sol should take ~10 hours to gel, and the resultant gel should be stable at that temperature for 6-34 years. However, at high EGS temperatures (275-300 °C), the resultant gel is not thermally stable for more than a few hours. This may in fact be beneficial for geothermal energy production, assuming that it is advantageous to preferentially block the relatively cold areas of the fracture network in order to maximize heat production.

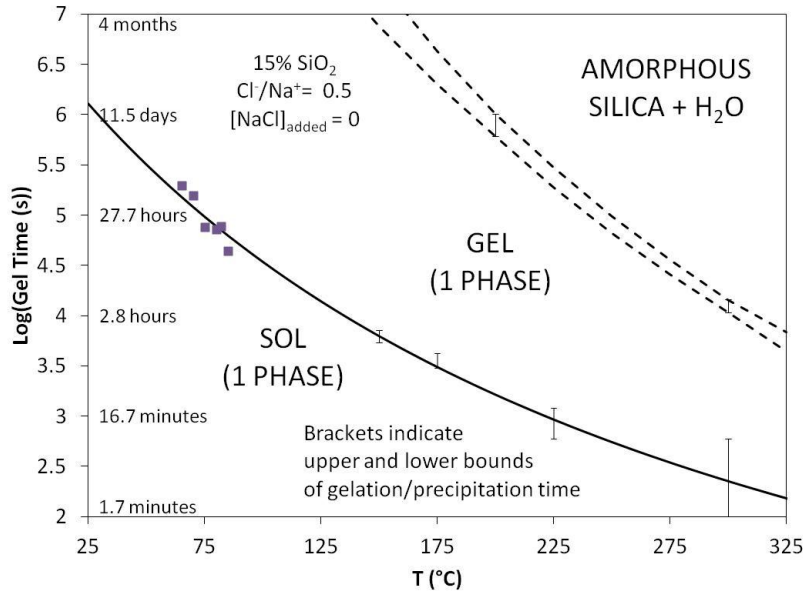


Figure 9: Gelation time and gel stability as a function of temperature

The model outlined by Eqs. 1-3, especially with the observation that the dependence of the logarithm of the gelation time on the logarithm of silica concentration is linear, can be used to predict gelation times of compositions that would take a prohibitively long time to gel at ambient conditions. Because of the Arrhenius relationship between gelation time and temperature, such a composition is necessary to provide a reasonable gelation time at EGS conditions. Further work will need to be done on other solution compositions at EGS conditions in order to provide a suite of gelation times and stabilities.

## CONCLUSIONS

We have made significant progress in the determination of a new candidate agent for blocking, diverting, or modifying fracture flow networks in EGS systems. Although more work at high temperature still needs to be done, results indicate that it is possible to choose formulations that will gel in a reasonable and predictable amount of time at the temperatures of EGS systems. We have also determined that shear rate does not impact the gelation time, which enables the prediction of gelation time within a fracture without regard for the physical circumstances of emplacement. We have determined that while colloidal gels are not stable for long periods of time at high temperatures, this is advantageous for EGS, as cold pathways can preferentially be blocked. Results from this study are informing concurrent work at LLNL on modeling fluid flow in rough fractures. The modeling work, illustrated in Figure 10, is proof-of-concept work of the positive impact of silica gel deployment. If the temperature of a pathway starts to decrease, the gel can be deployed in such a way as to divert the flow of water around the gelation zone, so that additional heat will be recovered from the fracture. LLNL's modeling effort is also addressing the uncertainty propagation, quantification and sensitivity analysis for large space parameters such as the one at hand and has begun implementation of the gelation process into a more realistic three dimensional fracture network.

Together, the experimental and modeling work will ultimately help increase the thermal energy production from EGS systems by altering the fracture permeability to create different zones of circulation that can be exploited in geothermal heat extraction.

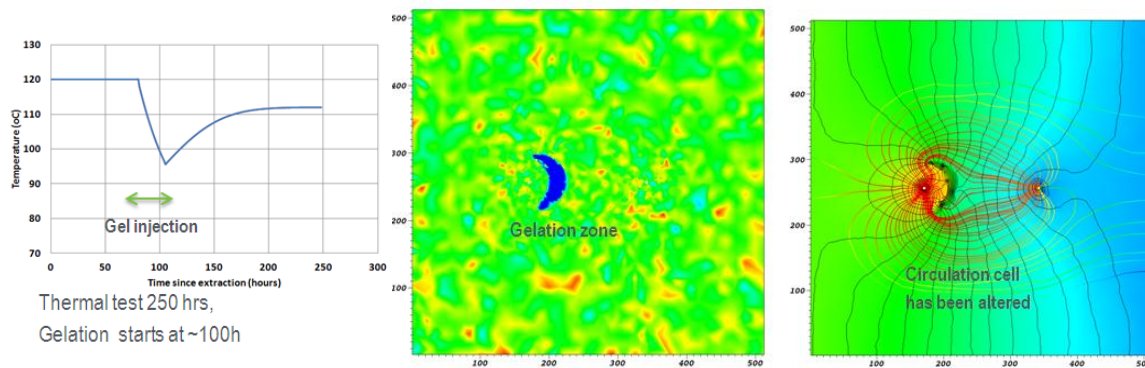


Figure 10: Two dimensional doublet flow and transport simulations of gel in a single rough fracture. Left: Temperature response at production well as a function of time. Center: Aperture field with gelled silica diverter. Right: Flow network showing the impact of silica gel on streamlines and flow cells.

## **ACKNOWLEDGEMENT**

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## **REFERENCES**

- Bergna H. E., and Roberts W. O., 2006. Colloidal Silica Fundamentals and Applications. Taylor and Francis.
- Bourcier, W. L., Bruton, C. J. and Gutierrez, P. (2008) Pilot-scale Geothermal Silica Recovery at Mammoth Lakes, California Energy Commission (CEC) PIER Final Report, Contract PIR-04-003.
- Ezzedine, S. M., Hunt, J. D., Bourcier, W., and Roberts, S. K., 2012. *Impact of Silica Gel Deployment on Subsurface Flow and Heat Extraction from Enhanced Geothermal Systems*, Annual Stanford Workshop on Geothermal Reservoir Engineering, Stanford, Feb 2012.
- Iler R. K., 1979. The Chemistry of Silica. Wiley.
- Jurinak, J. J., and Summers, L. E., 1991. *Oilfield Applications of Colloidal Silica Gel*. SPE Production Engineering, **6**, 406-412.
- Vossoughi, S., 2000. *Profile modification using in situ gelation technology – a review*. Journal of Petroleum Science and Engineering, **26**, 199-209.